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(54) Title: LOW BED-LEVEL TRANSITION, START-UP, AND REACTOR RESIDENCE TIME CONTROL USING SOUND WAVES (57) Abstract A process is provided for low bed level polymerization, using sound waves to prevent reactor fouling and/or sheeting. The process is useful during reactor start-up, polymer product transitioning, and for polymer residence time control in the reactor.		

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LOW BED-LEVEL TRANSITION, START-UP, AND REACTOR RESIDENCE TIME CONTROL USING SOUND WAVES**Field of the Invention**

The invention relates to olefin and/or diolefin polymerizations in a fluidized bed reactor. More particularly, the invention relates to the use of sonic cleaning devices and low-bed levels in reactor start-up, product transitioning, and reactor residence time control for polymerization of these polymers.

Background of the Invention

One of the most economic and commonly used methods to manufacture polyolefins is gas phase polymerization. A conventional gas phase fluidized bed reactor used in polymerizing olefins and/or diolefins contains a fluidized dense-phase bed (i.e., the mixture of reaction gas and polymer (resin) particles) and a freeboard above the dense-phase surface (bed level). The freeboard contains mainly gas and a small amount of particles, especially the fine particles (fines). The dense-phase bed is usually maintained in a cylindrical straight section of the reactor. Above the straight section, there is a section having a larger diameter, the so-called expanded section, to reduce the gas velocity for the purpose of reducing the amount of fines carried out of the reactor to other parts of the reaction system. The expanded section connects with the straight section by its tapered conical section. The freeboard is usually located at the expanded section. If the bed level is lower than the top of the straight

- 2 -

section, the upper portion of the straight section also becomes a part of the freeboard.

During the reactor operation, fines present in the freeboard can be carried away by the gas leaving the reactor or fall back into the dense-phase bed. However, some fines may attach on the interior wall of the reactor system, particularly in the freeboard portion, and accumulate to form so called sheets, i.e., layers of agglomerated or melted or half-melted resin and catalyst particles. Sheets can adversely affect properties of the polymer product. When sheets become heavy, they can fall off the walls and plug the product discharge system or clog the distributor plate. The relatively small pieces of sheets can be discharged together with the bulk resin particles and contribute to product quality problems by increasing the gel level in end-use products such as plastic containers and films. Sheeting and fines accumulation are collectively referred to as solid particle build-up. Proper operating conditions are needed to prevent solid particle build-up on the interior wall of the reactor freeboard.

During normal operations, the bed level of the fluidized bed polymerization reactor is usually maintained close to the top of the straight section. In this way, the lower portion of the conical section can be cleaned by the "scrubbing effect" of particles thrown out by bursting bubbles. The other portions of the expanded section are usually free of solid particle build-up, due to low particle concentrations in these areas, and as a result of the particle carry-away from reactor wall by drag force of the cycle gas. If the bed level is lower than the top of the straight section, the upper part of the straight section and the lower part of the conical section can not be protected by the "scrubbing effect" contributed by the bed-level fluctuation. Thus,

- 3 -

severe solid particle build-up, usually with catalyst rich fines, can be encountered in those locations.

For a given fluidized bed polymerization reactor, maintaining the bed level close to the top of the straight section means the reactor inventory is fixed. Under certain circumstances a smaller or variable reactor inventory is desired, such as for reactor start-up, product transition, and reactor residence time control.

When the reactor is started-up, the bed is filled with a "seed bed" that consists of previously made resin particles generally similar to the product particles to be made in the reactor. Since the seed particles are usually not exactly the same as the product particles, off-grade resin particles can be made during the start-up of the reactor. When almost all the seed particles have been discharged, the reactor starts to discharge the aim-grade product. Thus, at reactor start-up, operation with low bed level can significantly reduce the amount of the off-grade product.

During a product transition, the reactor operating conditions are changed to produce the desired product. Similar to the reactor start-up, a large quantity of off-grade product can be produced during the transition until almost all the previous product has been discharged. Obviously, the low bed-level operation (i.e., the low reactor inventory) can benefit the product transition by significantly reducing the amount of the off-grade product.

Even during the normal operation, the variation of the reactor residence time is often required for the purpose of producing specific products. For many polyolefin products, the product properties are strongly related to the polymer residence time in the reactor. If the reactor inventory is fixed due to a bed level requirement, the

- 4 -

production rate has to be adjusted to change the polymer residence time. However, such an adjustment could adversely affect the reactor operation, and the adjustment can be limited by other factors such as product discharge capacity, catalyst feeding rate, or downstream facility capacity. On the other hand, if the bed level can be reduced, reactor residence time can be easily varied to meet the requirement for product properties without affecting the production rate.

U.S. Patent No. 5,461,123 discloses a process for protecting reactor walls from particle build-up by the use of sound waves. According to that invention, sound waves are introduced by the sonic cleaning devices into the reactor to loosen particles on the walls. The loosened particles can be carried away from the wall by gravity or by drag forces.

There is a need to provide an improved gas phase fluidized bed polymerization process with the capability to operate at low bed levels without causing additional operating problems such as particle build-up on the wall.

Summary of the Invention

Accordingly, there is provided a process for (1) the reduction of off-grade product during reactor start-up, (2) the reduction of off-grade product during transitioning from a first product to a second product, or (3) shortening a polymer residence time while essentially maintaining other operating conditions constant, comprising: polymerizing (a) at least one alpha olefin and optionally a diene or (b) at least one diolefin in the presence of at least one polymerization catalyst in a fluidized bed reactor having a freeboard section and a dense bed section by introducing sound waves into the

- 5 -

reactor while the dense phase bed section is lowered to or maintained at a reduced level.

Brief Description of the Drawing

Figure 1 is a depiction of a conventional gas phase reactor. In Figure 1, a conventional gas phase fluidized bed reactor (1) used in polymerizing alpha-olefins contains a fluidized dense-phase bed (2), i.e., the mixture of reaction gas, polymer (resin) particles and catalyst(s), and a freeboard (3) above the dense-phase bed level (4). The freeboard contains mainly gas and a small amount of particles, especially the fine particles (fines). The dense-phase bed is usually maintained in a cylindrical straight section (5) of the reactor, with the bed-level near the top of that straight section. Above the straight section there is a section with larger diameter, a so-called expanded section (6), to reduce the gas velocity for the purpose of reducing the amount of fines carry-out from the reactor. The expanded section connects with the straight section by its tapered conical section (7). If the bed level is lower than the top of the straight section, the upper portion of the straight section also becomes a part of the freeboard. The whole dense phase bed is usually supported by a gas distribution plate (8) located at the bottom of the straight section.

Figure 2 is a schematic of a sound wave producing device and its interfaces with a reactor wall. In Figure 2, 1=pulsation generation unit; 2=sonic tube; 3=exterior wall of the reactor; 4=interior wall of the reactor; and 5=sonic nozzle.

Detailed Description of the Invention

Polymers and Monomers. Illustrative of the polymers which can be produced in accordance with the process of the invention are the following: homopolymers and copolymers of C₂-C₁₈ alpha olefins; polyvinyl chlorides, ethylene propylene rubbers (EPRs); ethylene-propylene diene rubbers (EPDMs); polyisoprene; polystyrene; polybutadiene; polymers of butadiene copolymerized with styrene; polymers of butadiene copolymerized with isoprene; polymers of butadiene copolymerized with acrylonitrile; polymers of isobutylene copolymerized with isoprene; ethylene butene rubbers and ethylene butene diene rubbers; polychloroprene; norbornene homopolymers and copolymers with one or more C₂-C₁₈ alpha olefin; terpolymers of one or more C₂-C₁₈ alpha olefins with a diene; and the like.

Monomers that can be employed in the process can include one or more: C₂ to C₁₈ alpha olefins such as ethylene, propylene, and optionally at least one diene (such as those taught in U.S. Patent No. 5,317,036 to Brady et al.), for example, hexadiene, dicyclopentadiene, octadiene including methyloctadiene (e.g., 1-methyl-1,6-octadiene and 7-methyl-1,6-octadiene), norbornadiene, and ethylidene norbornene; readily condensable monomers such as those taught in U.S. Patent No. 5,453,471 including isoprene, styrene, butadiene, isobutylene, chloroprene, acrylonitrile, cyclic olefins such as norbornenes, and the like.

Polymerization Process. The process of the present invention can be used in conjunction with slurry, solution, bulk, stirred bed and fluidized bed polymerizations. The interior surfaces above the dense-phase (including gas-solid dense phase, slurry phase, or solution phase) level in any one of those reactors can be protected by the use of

- 7 -

sound wave producing device(s) in accordance with this invention to prevent the particle accumulation. Even the surfaces under the dense-phase level can also be partially or completely protected, especially when liquid exists in the dense phase.

Preferably, the present invention is employed in fluidized bed polymerizations, most preferably those utilizing a gas phase. The present invention is not limited to any specific type of fluidized or gas phase polymerization reaction and can be carried out in a single reactor or multiple reactors (two or more reactors in series). In addition to well known conventional gas phase polymerizations processes, "condensing mode", including the so-called "induced condensing mode", and "liquid monomer" operation of a gas phase polymerization can be employed.

A conventional fluidized bed process for producing resins is practiced by passing a gaseous stream containing one or more monomers continuously through a fluidized bed reactor under reactive conditions in the presence of a polymerization catalyst. Product is withdrawn from the reactor. A gaseous stream of unreacted monomer is withdrawn from the reactor continuously and recycled into the reactor along with make-up monomer added to the recycle stream. Conventional gas phase polymerizations are disclosed, for example, in U.S. Patent Nos. 3,922,322; 4,035,560; and 4,994,534.

Condensing mode polymerizations are disclosed in U.S. Patent Nos. 4,543,399; 4,588,790; 4,994,534; 5,352,749; and 5,462,999. Condensing mode processes are employed to achieve higher cooling capacities and, hence, higher reactor productivity. In these polymerizations a recycle stream, or a portion thereof, can be cooled to a temperature below the dew point in a fluidized bed polymerization

- 8 -

process, resulting in condensing all or a portion of the recycle stream. The recycle stream is returned to the reactor. The dew point of the recycle stream can be increased by increasing the operating pressure of the reaction/recycle system and/or increasing the percentage of condensable fluids and decreasing the percentage of non-condensable gases in the recycle stream. The condensable fluid may be inert to the catalyst, reactants, and the polymer product produced. It may also include monomers and comonomers. The condensing fluid can be introduced into the reaction/recycle system at any point in the system. Condensable fluids include saturated or unsaturated hydrocarbons.

In addition to condensable fluids of the polymerization process itself, other condensable fluids inert to the polymerization can be introduced to "induce" condensing mode operation. Examples of suitable condensable fluids may be selected from liquid saturated hydrocarbons containing 2 to 8 carbon atoms (e.g., ethane, propane, n-butane, isobutane, n-pentane, isopentane, neopentane, n-hexane, isohexane, and other saturated C₆ hydrocarbons, n-heptane, n-octane and other saturated C₇ and C₈ hydrocarbons, and mixtures thereof). Condensable fluids may also include polymerizable condensable comonomers such as olefins, alpha-olefins, diolefins, diolefins containing at least one alpha olefin, and mixtures thereof. In condensing mode, it is desirable that the liquid entering the fluidized bed is dispersed and vaporized quickly.

Liquid monomer polymerization mode is disclosed, in U.S. Patent No. 5,453,471; U.S. Serial No. 08/510,375; PCT 95/09826 (US) and PCT 95/09827 (US). When operating in the liquid monomer mode, liquid can be present throughout the entire polymer bed provided that the liquid monomer present in the bed is adsorbed on or absorbed in

- 9 -

solid particulate matter present in the bed, such as polymer being produced or inert particulate materials (e.g., carbon black, silica, clay, talc, and mixtures thereof) present in the bed, so long as there is no substantial amount of free liquid monomer present. Liquid mode makes it possible to produce polymers in a gas phase reactor using monomers having condensation temperatures much higher than the temperatures at which conventional polyolefins are produced. In general, a liquid monomer process is conducted in a stirred bed or gas fluidized bed reaction vessel having a polymerization zone containing a bed of growing polymer particles. The process comprises continuously introducing a stream of one or more monomers and optionally one or more inert gases or liquids into the polymerization zone; continuously or intermittently introducing a polymerization catalyst into the polymerization zone; continuously or intermittently withdrawing polymer product from the polymerization zone; continuously withdrawing unreacted gases from the zone; and compressing and cooling the gases while maintaining the temperature within the zone below the dew point of at least one monomer present in the zone. If there is only one monomer present in the gas-liquid stream, there is also present at least one inert gas. Typically, the temperature within the zone and the velocity of gases passing through the zone are such that essentially no liquid is present in the polymerization zone that is not adsorbed on or absorbed in solid particulate matter.

Typically, the fluidized bed polymerization process is conducted at a pressure ranging from about 10 to 1000 psi, preferably about 200 to about 600 psi and a temperature ranging from about

- 10 -

10 °C to about 150 °C, preferably about 40 °C to about 125 °C. During the polymerization process the superficial gas velocity ranges from about 0.7 to 3.5 feet/second, and preferably about 1.0 to 2.7 feet/second.

Catalysts. Any type of polymerization catalyst may be used in the polymerization process of the present invention. A single catalyst may be used, or a mixture of catalysts may be employed, if desired. The catalyst can be soluble or insoluble, supported or unsupported. It may be a prepolymer, spray dried with or without a filler, a liquid, or a solution, slurry or dispersion. These catalysts are used with cocatalysts and promoters well known in the art. Typically these are alkylaluminums, alkylaluminum halides, alkylaluminum hydrides, as well as aluminoxanes. For illustrative purposes only, examples of suitable catalysts include:

- A. Ziegler-Natta catalysts, including titanium based catalysts such as those described in U.S. Patent Nos. 4,376,062 and 4,379,758.
Ziegler-Natta catalysts are well known in the art, and typically are magnesium/titanium/electron donor complexes used in conjunction with an organoaluminum cocatalyst.
- B. Chromium based catalysts such as those described in U.S. Patent Nos. 3,709,853; 3,709,954; and 4,077,904.
- C. Vanadium based catalysts such as vanadium oxychloride and vanadium acetylacetonate, such as described in U.S. Patent No. 5,317,036 and 5,585,184.
- D. Metallocene catalysts and other single-site or single-site-like catalysts such as those taught in U.S. Patent Nos. 4,530,914; 4,665,047; 4,752,597; 5,218,071; 5,272,236; 5,278,272; 5,317,036; 5,585,184; and 5,527,752.

- 11 -

- E. Cationic forms of metal halides, such as aluminum trihalides.
- F. Anionic Initiators such as butyl lithiums.
- G. Cobalt catalysts and mixtures thereof such as those described in U.S. Patent Nos. 4,472,559; 4,182,814; and WO 96/04322.
- H. Nickel catalysts and mixtures thereof such as those described in U.S. Patent Nos. 4,155,880; 4,102,817; and WO 96/04322.
- I. Rare earth metal catalysts, i.e., those containing a metal having an atomic number in the Periodic Table of 57 to 103, such as compounds of cerium, lanthanum, praseodymium, gadolinium and neodymium. Especially useful are carboxylates, alcoholates, acetylacetonates, halides (including ether and alcohol complexes of neodymium trichloride), and allyl derivatives of such metals, e.g., of neodymium. Neodymium compounds, particularly neodymium neodecanoate, octanoate, and versatate, and n-alkyl neodymium are the most preferred rare earth metal catalysts. Rare earth catalysts are especially preferred and used to produce polymers polymerized using butadiene, styrene, or isoprene and the like as disclosed in WO 96/04323.

Preferred catalysts for the process of the present invention include rare earth metal catalysts, titanium catalysts, chromium catalysts, vanadium catalysts, nickel catalysts, and the metallocene/single-site/single-site-like catalysts.

Inert Particulate Materials. Additionally, the polymerization process of the present invention can include inert particulate materials. Inert particulate materials can include, for example, carbon black, silica, clay, and talc used during the production of sticky polymers and diolefin polymerizations. The employment of inert particulate materials is disclosed, for

- 12 -

example, in U.S. Patent Nos. 5,317,036; 4,994,534; and 5,453,471. Of the inert particulate materials, carbon black, silica, and a mixture thereof are preferred, with carbon black being most preferred. When utilized, the inert particulate material is employed in the gas-phase polymerization in an amount ranging from about 0.3 to about 80 weight percent, preferably about 5 to about 75 weight percent, most preferably 5 to 50 weight percent based on the weight of the final polymer product.

Sonic Waves and Sound Wave Producing Devices (Sonic Cleaners). In the present invention, sound waves are generated by one or more sound wave producing devices (also referred to herein as sonic cleaners). The sound wave producing device includes at least one pulsation generation unit, at least one sonic tube connected with the pulsation generation unit to generate and propagate the sound waves at the desired frequency, and at least one sonic nozzle at the end of the sonic tube to introduce the sound waves into the reactor. The pulsation generation unit typically includes one or more chambers containing at least one piston moving back-and-forth in the same frequency as the sonic frequency, with the piston(s) driven by gas, electric, or other means. The pulsation generation unit is available from Kockum-Sonics AB (Sweden). The sound waves can be introduced into the reactor via sonic nozzles positioned in one or more locations above the bed level. Suitable sonic wave producing devices are disclosed, for example, in U.S. Patent No. 5,462,123 and EPO 189 386 A3. A horn is also a special type of the sound wave producing unit, with a size-varying "sonic tube" and its open-end working as the "sonic nozzle." A horn is commercially available, e.g., from Kockum-Sonics AB (Sweden).

- 13 -

The sound energy introduced by the sound wave producing device(s) has to be able to dislodge polymer particles, fines, sheets or other particles from the inside surfaces of the reactor system. A parameter called Standard Sound Pressure Level (SSPL) is used herein to measure the energy level of a sound wave producing device. SSPL is defined as the Sound Pressure Level (SPL) measured at 1 meter away from a sound source (e.g., sonic nozzle) in the absence of obvious interference contributed by the reflected sound waves. The SSPL of the sound wave producing device employed in the present invention is preferably from about 100 to 200 decibels (dB), and most preferably from about 140 dB to 170 dB.

The interior surface of the reactor system to be cleaned, e.g., the surface in the reactor freeboard section, can be protected by the sound waves with sufficient energy to prevent particle accumulation. The SPLs at different locations of the surface to be cleaned are usually different due to different distances from the sonic nozzle(s), etc. Thus, the minimum Sound Pressure Level (mSPL) on the entire surface to be cleaned is an index to measure the effectiveness of the sound waves in preventing solid particle build-up. In the present invention, the minimum SPL on the entire surface to be cleaned in the reactor system is preferably from about 100 dB to 200 dB, and most preferably from about 120 to 170 dB.

Sound waves employed in the present invention are of a frequency suitable to dislodge polymer particles, fines, sheets or other particles from the interior surfaces of the reactor system. When the frequency is too high, the particles attached on the reactor wall would be difficult to loosen. When the frequency is too low, the sonic tube used to generate the sound wave would be too long and cause

- 14 -

undesirable sound energy loss. The sound wave frequency used in the present invention can vary from the non-audible infrasonic wave range (with a typical sound frequency lower than 20 Hertz (Hz)) to the audible sonic wave range (with a typical sound frequency higher than 20 Hz). The frequency is preferably from about 5 to 40 Hz, and most preferably from about 10 to 25 Hz.

Duration and interval of the sound waves are indexes used to determine sonic cleaner performance. Duration is the period of time that the device is producing sound waves, and interval is the period of time between two adjacent activations of the sonic device. A long interval may result in undesirable levels of solid particle build-up on the reactor wall and cause difficulties in cleaning the wall by sound waves. A short duration may not achieve sufficient cleaning effect. In the present invention, the preferred interval of the sonic cleaner is from about zero (i.e., continuous operation) to 4 hours, most preferably from about 3 minutes to 1 hour. The optimum duration employed in the present invention is preferably from about 5 seconds to continuous operation, most preferably from about 10 to 60 seconds.

The optimal number of the sonic nozzles depends on the total volume of the reactor freeboard. The ratio of freeboard volume, in cubic feet, to nozzle number used in the present invention is preferably less than about 7,000 cubic feet per nozzle, and most preferably less than about 5,000 cubic feet per nozzle.

Reactor Residence Time Control. The reactor production rate is defined as the amount of polymer produced per unit time. Thus, the average residence time of resin particle in the reactor (τ) can be expressed as

- 15 -

$$\tau = \frac{V \text{ FBD}}{R} \quad (1)$$

where V is the bed volume below the bed level, FBD is the fluidized bulk density, and R is the production rate. It can be seen from Eq.(1) that if it is not desired to substantially change the production rate or the fluidized bulk density, the only way to reduce the reactor residence time is by reducing the bed volume, i.e., reducing the bed level.

Whenever a short residence time in the reactor is desired to maintain certain product properties such as crystallinity, gel level and elongation at break of the elastomers, the bed level can be reduced to a proper level to achieve the desired residence time by the present invention without changing other operating conditions. The sonic cleaner is utilized during the entire period of the low-bed level operation to ensure that no particle build-up occurs on the interior wall of the reactor freeboard, especially in the upper part of the straight section and lower part of the conical section. Even when the low bed level is no longer needed, the sonic cleaner can still be kept on to make sure the freeboard surface is protected.

Low Bed-Level Reactor Start-up. During reactor start-up, a seed bed is employed. As the reaction is established and fresh polymer particles are made, the seed particles are gradually discharged from the reactor together with the fresh product particles. Due to the solid mixing pattern of the fluidized bed reactor, it takes long time of operation to replace almost all seed bed particles by the aim-grade product. The mixture of seed particles and product particles is normally treated as off-grade product. It is desired to use as small amount of seed particles as possible.

- 16 -

The present invention allows the bed level of seed particles to be substantially lower than the top of the straight section of the reactor. Sonic cleaner(s) are used to protect the whole freeboard surfaces, especially the upper part of the straight section and lower part of the conical section, from particle build-up.

According to the present invention, the bed level is maintained at a low level during the reactor start-up until almost all the seed particles have been discharged and the product has reached aim-grade. The bed level can then be gradually raised until it is close to the top of the straight section, and thereafter normal production is resumed. The sonic cleaner can be kept in service, if desired, after the start-up is finished. The ratio of the low bed level to the normal bed level is approximately the ratio of off-grade product produced during low bed-level start-up to that produced during normal bed-level start-up. In this way, the amount of the off-grade product can be reduced, and start-up time can be shortened.

In the present invention, the bed level during the reactor start-up is preferably to be lowered to about 1% to 80% of the full bed level, and most preferably to be 25% to 60% of the full bed level.

Low Bed-Level Product Transition. The most economical and commonly used method for the transition from Product A (a first product) to a Product B (a second product) is to change the reaction conditions from those needed to make Product A to those needed to make Product B without shutting down the reactor. As reaction conditions are changed to produce Product B, the bed gradually becomes a mixture of Product A and Product B, due to the solid mixing pattern in the fluidized bed. Before all Product A particles are discharged, the intermediate product of the reactor is usually an off-

- 17 -

grade one, i.e., a mixture of Products A and B. If the quantity of Product A particles in the reactor is smaller prior to the transition, less off-grade products will be made.

The present invention allows the low bed-level product transition to generate less off-grade product. Reduced off-grade product during transition is accomplished by:

- (a) lowering the bed level at the end of Product A production, and activating the sonic cleaner(s) to protect the freeboard surfaces;
- (b) changing reaction conditions from those for Product A to those for Product B, and maintaining the bed level at the lowered position while the sonic cleaner(s) are still in service;
- (c) after essentially all Product A particles are discharged from the bed, the bed level is gradually increased to the normal position, and the normal Product B production is continued.

In this way, less off-grade product is generated during product transition, and product transition time is shortened. The sonic cleaner can be kept running even after the product transition is finished.

In the present invention, the bed level during the product transition is preferably to be lowered to about 1% to 90% of the full bed level, and most preferably to be 25% to 60% of the full bed level.

All patents mentioned in the specification are hereby incorporated by reference.

The invention is further illustrated by the following examples.

Examples

Examples 1-5: Reactor Residence Time Control and Product Properties

Examples 1 and 2 illustrate the effect of residence time on product properties. Examples 3 and 4 illustrate the effect of bed level on solid particle build-up on the interior wall of the reactor. Example 5 shows that using a sonic cleaner to prevent particle build-up with a low bed level will allow the residence time to be controlled independently of production rate which in turn allows control of product properties independent of production rate.

A fluidized bed gas phase reaction system with the reactor configuration similar to the one shown in Fig. 1 to produce an ethylene-propylene-diene terpolymer is utilized in Examples 1-5. The results for Examples 1 through 4 are reported in Tables 1 and 2. The catalyst was vanadium tris-acetylacetonate supported on silica (Type 958 supplied by W. R. Grace, Davison Silica Division and dehydrated at about 600°C). The catalyst feed was controlled at a rate to have a production rate that results in the desired polymer residence time. A co-catalyst mixture of 5:1 diethyl aluminum chloride:triethyl aluminum and a promoter of ethyl trichloroacetate were fed separately to the reactor. Carbon black (N-650 beads supplied by Columbian Chemicals Company) was used as an inert particulate material or fluidization aid for producing polymer above its softening point. The carbon black was heated and purged with nitrogen prior to feeding to the reactor to remove absorbed water and oxygen which are poisons for the catalyst. Reaction conditions and results are summarized in Tables 1 and 2. Elongation was measured in accordance with ASTM-D412.

- 19 -

Example 1. Example 1 illustrates operation with a long residence time of 4.8 hours. The product had a high level of total crystallinity (5.1%) and a low elongation at break (371%).

Example 2. Example 2 (comparative) illustrates operation with a short residence time of 2.9 hours. The product had a low level of total crystallinity (2.9%) and a high elongation at break (523%).

Example 3. Example 3 illustrates operation with a bed level at the top of the straight section. The reactor operated for greater than 10 days with no particle build-up in the straight section and lower conical section.

Example 4. Example 4 (comparative) illustrates operation with a bed level 3 feet below the top of the straight section. A solid build-up layer several inches thick formed on the wall of the straight section above the bed level and in the lower conical section after 1 day of operation. In addition, polymer-carbon black chunks of approximately 0.25 to 0.75 inches fell into the bed and were discharged with the product.

Example 5. All the conditions are identical to those of Example 4, except a sonic cleaner is employed. The sonic nozzle is located at the expanded section of the reactor with SSPL of about 150 dB and minimum SPL of about 140 dB in the entire expanded section and the straight section above the bed level. The sound frequency is about 16.5 Hz and the sonic cleaner is activated for about 15 seconds approximately every 10 minutes. Continuous operation is maintained for 10 days without particle build-up on the freeboard surface.

Example 6: Commercial Scale Product Transition. A gas phase fluidized bed polyolefin reaction system containing a fluidized bed volume of about 6,900 cubic feet containing about 127,500 pounds

- 20 -

of polymer resin is employed. The reactor is operated at a production rate of about 42,500 pounds per hour or about 3-hour residence time. The reaction system produces a polyethylene product having a melt index of 2 g/10 min and a density of 0.924 g/cm³ using a titanium based catalyst and an aluminum alkyl co-catalyst while operating at the following conditions:

Reactor pressure:	300 psig
Reactor temperature:	91 °C
Ethylene partial pressure:	110 psia
1-Hexene to ethylene molar ratio	0.105
Hydrogen to ethylene molar ratio:	0.186

In order to make a transition to a different grade polymer product, having a melt index of 5 g/10 min and a density of 0.934 g/cm³, three sonic cleaners with an SSPL of 152 dB, mounted 120° from each other and flush with the wall in the middle of the reactor conical section, are activated for about 15 seconds approximately every 10 minutes with the sound frequency about 17 Hz. Once it is evident that there is no accumulation of fines in the expanded section as indicated by the expanded section skin thermocouples, the fluidized bed level is lowered slowly to about 50% of the normal operating level, while maintaining a constant production rate. After the bed level reaches the 50% normal operating level, the conditions in the reactor are adjusted as follows to make the next polyethylene product having a melt index of 5 g/10 min and a density of 0.934 g/cm³:

- 21 -

Reactor pressure:	300 psig
Reactor temperature:	96 °C
Ethylene partial pressure:	160 psia
1-Hexene to ethylene molar ratio	0.069
Hydrogen to ethylene molar ratio:	0.290

Once these conditions are achieved in the reactor, and the product reaches specifications, the bed level is returned to the normal operating level to complete the grade transition. The sonic cleaner makes it possible to do a grade transition in about 6 hours as compared to the 12 hours commonly practiced. In addition, the quantity of off-grade polymer produced during the grade transition is reduced by approximately 50%.

Example 7: Commercial Scale Reactor Start-up. The same reactor and sonic cleaners of Example 6 are used. The target product is a polyethylene product having a melt index of 1 g/10 min and a density of 0.918 g/cm³ using a titanium based catalyst and an aluminum alkyl co-catalyst while the target operating conditions are:

Reactor pressure:	308 psig
Reactor temperature:	88 °C
Ethylene partial pressure:	125 psia
1-Hexene to ethylene molar ratio	0.090
Hydrogen to ethylene molar ratio:	0.323

The start-up follows the regular start-up procedures of the fluidized bed polymerization reactor, except the fluidized seed bed level is about 50 % of the normal operating level. Sonic cleaners are used in the entire period of the start-up, with the operating parameters

- 22 -

identical to those of Example 6. Once the target operating conditions are achieved in the reactor, and the discharged product reaches specifications, the bed level is increased to the normal operating level to complete the reactor start-up. The sonic cleaner makes it possible to reach aim-grade product in less time that is commonly taken. In addition, the quantity of off-grade polymer produced during the grade transition is reduced.

Table 1

	Example 1	Example 2
	Long Residence Time	Short Residence Time
CATALYST TYPE	Vanadium Tris-Acetylacetonate	Vanadium Tris-Acetylacetonate
REACTION CONDITIONS		
Residence Time, hrs	4.8	2.9
Temperature, °C	40	40
Pressure, psia	369	364
Hydrogen/Ethylene volume ratio	0.011	0.014
Propylene/Ethylene volume ratio	2.01	2.08
ENB, gas phase ppm by volume	9.9	8.2
Ethylene Partial Pressure, psia	80	80
Superficial Gas Velocity, ft/sec	1.5	1.5
Inert Particulate Material (Carbon Black)	Columbian Statex® N-650 Beads	Columbian Statex® N-650 Beads
PARTICLE SIZE		
Weight Average Particle Size, inches	0.038	0.037
RESIN PROPERTIES		
Inert Particulate Material, wt. %	19.3	20.9
Mooney Viscosity, ML(1+4), 125°C	77	76
Propylene, Polymer wt. % by IR	31.6	30.4
ENB, Polymer wt. % by IR	2.15	1.86
Crystallinity, wt. % by DSC	5.1	2.9
Percent Elongation at Break	371	523

- 23 -

Table 2

	Example 3 Bed Level at Top of Straight Section	Example 4 Low Bed Level
CATALYST TYPE	Vanadium Tris- Acetylacetonate	Vanadium Tris- Acetylacetonate
REACTION CONDITIONS		
Bed Level	at top of straight section	3 ft below the top of straight section
Residence Time, hrs	4.85	5.8
Temperature, °C	40	40
Pressure, psia	364	336
Hydrogen/Ethylene volume ratio	0.030	0.030
Propylene/Ethylene volume ratio	1.45	1.45
ENB, gas phase ppm by volume	18	10
Ethylene Partial Pressure, psia	80	80
Superficial Gas Velocity, ft/sec	1.5	1.6
Inert Particulate Material (Carbon Black)	Columbian Statex® N-650 Beads	Columbian Statex® N-650 Beads
PARTICLE SIZE		
Weight Average Particle Size, inches	0.030	0.039
RESIN PROPERTIES		
Inert Particulate Material, wt. %	21.5	23.3
Mooney Viscosity, ML(1+4), 125°C	60.0	63.2
Propylene, Polymer wt. % by IR	26.5	25.7
ENB, Polymer wt. % by IR	4.96	3.23

- 24 -

What is claimed is:

1. A process for (1) the reduction of off-grade product during reactor start-up, (2) the reduction of off-grade product during transitioning from a first product to a second product, or (3) shortening a polymer residence time while essentially maintaining other operating conditions constant, comprising: polymerizing (a) at least one alpha olefin and optionally a diene or (b) at least one diolefin in the presence of at least one polymerization catalyst in a fluidized bed reactor having a freeboard section and a dense bed section by introducing sound waves into the reactor while the dense phase bed section is lowered to or maintained at a reduced level.

2. The improved process of Claim 1 wherein the sound waves are produced using sound wave devices having at least one pulsation generation unit, at least one sonic tube connected to the pulsation generation unit, and at least one sonic nozzle at the end of the sonic tube to introduce sound waves into the reactor.

3. The improved process of Claim 1 wherein the sound wave producing devices emit a sound wave ranging from about 5 Hz to 40 Hz; and have a standard sound pressure level ranging from about 100 to 200 dB.

4. The improved process of Claim 1 wherein sound waves are introduced into a reactor in one or more locations in the freeboard section of the reactor.

- 25 -

5. The improved process of Claim 1 wherein the minimum sound pressure level on the entire surface to be protected by sound waves ranges from about 100 to 200 dB.

6. The improved process of Claim 2 wherein the ratio of reactor freeboard volume to number of sonic nozzles is less than about 7,000 cubic feet per nozzle.

7. The improved process of Claim 1 wherein the sound wave duration ranges from about 5 seconds to continuous operation, and the interval between two adjacent sonic activations ranges from about zero to 4 hours.

8. The process of Claim 1 wherein the bed level is lowered to about 1% to 90% of the full bed level.

9. The improved process of Claim 1 wherein an inert particulate material selected from the group consisting of carbon black, silica, clay, talc, and mixtures thereof is employed in the polymerization.

10. The improved process of Claim 1 wherein the polymer produced is selected from the group consisting of

- (a) homopolymers and copolymers of C₂-C₁₈ alpha olefins;
- (b) ethylene-propylene-diene terpolymers;
- (c) polybutadiene;

- 26 -

- (d) polyisoprene;
- (e) polystyrene;
- (f) polychloroprene;
- (g) polymers of butadiene copolymerized with styrene or isoprene;
- (h) polymers of butadiene copolymerized with acrylonitrile;
- (i) polymers of isobutylene copolymerized with isoprene; and
- (j) ethylene-butene rubbers and ethylene-butene-diene rubbers.

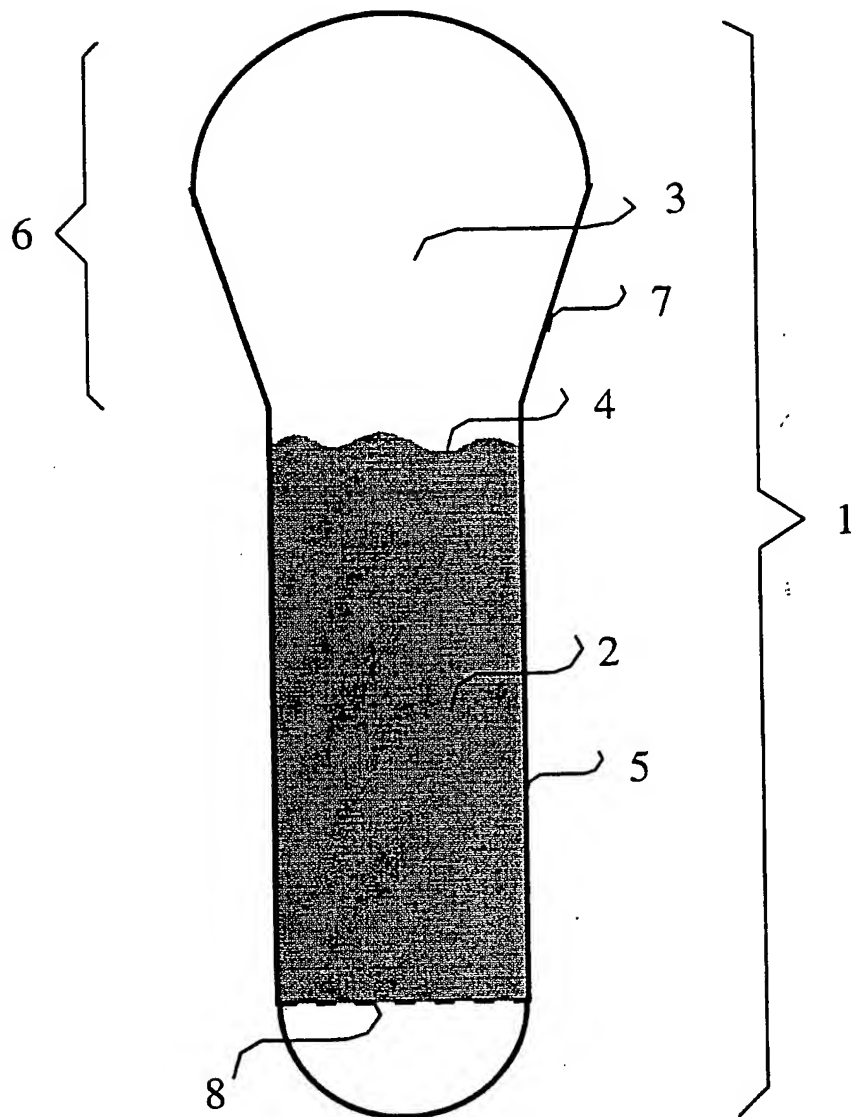


Figure 1

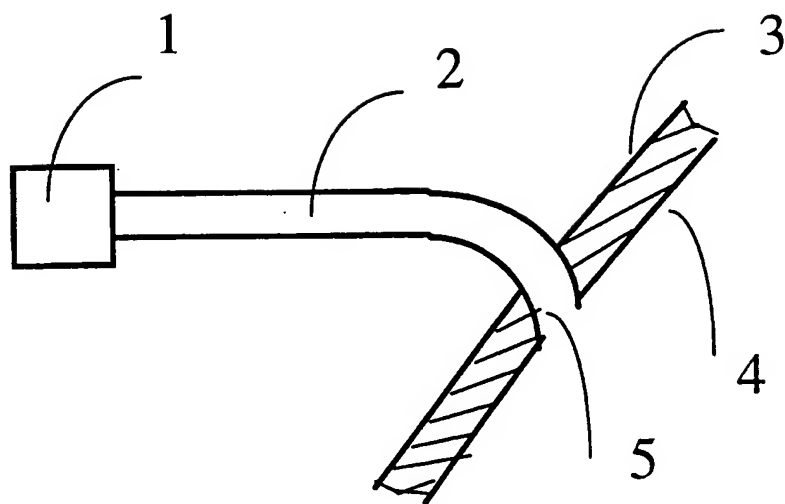


Figure 2

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 98/14673

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C08F10/00 C08F36/00 C08F2/34

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 461 123 A (SONG GYUNG-HO ET AL) 24 October 1995 cited in the application see the whole document ---	1-10
A	US 5 453 471 A (SCAROLA LEONARD S ET AL) 26 September 1995 cited in the application see claims ---	1-10
A	US 4 994 534 A (RHEE SEUNG J ET AL) 19 February 1991 cited in the application see claims -----	1-10

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 98/14673

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5461123 A	24-10-1995	AT 170535 T	15-09-1998
		AU 686383 B	05-02-1998
		AU 2498195 A	25-01-1996
		BR 9503324 A	30-04-1996
		CA 2153916 A,C	15-01-1996
		DE 69504438 D	08-10-1998
		EP 0692500 A	17-01-1996
		JP 8169915 A	02-07-1996
US 5453471 A	26-09-1995	AU 691957 B	28-05-1998
		AU 3211395 A	04-03-1996
		AU 687604 B	26-02-1998
		AU 3211495 A	04-03-1996
		AU 692586 B	11-06-1998
		AU 3237395 A	04-03-1996
		BR 9503534 A	16-04-1996
		BR 9508515 A	21-10-1997
		BR 9508517 A	21-10-1997
		CA 2196664 A	15-02-1996
		CN 1133298 A	16-10-1996
		CN 1158624 A	03-09-1997
		CN 1171793 A	28-01-1998
		CZ 9700296 A	11-06-1997
		CZ 9700297 A	11-06-1997
		CZ 9700320 A	11-06-1997
		EP 0697421 A	21-02-1996
		EP 0773964 A	21-05-1997
		EP 0773963 A	21-05-1997
		EP 0773965 A	21-05-1997
		EP 0856531 A	05-08-1998
		EP 0856530 A	05-08-1998
		HU 76682 A	28-10-1997
		JP 8100009 A	16-04-1996
		JP 10503799 T	07-04-1998
		JP 10503800 T	07-04-1998
		NO 970464 A	21-03-1997
		PL 318524 A	23-06-1997
		PL 318526 A	23-06-1997
		PL 318527 A	23-06-1997
		SK 14897 A	10-09-1997

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 98/14673

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5453471 A		WO 9604322 A	15-02-1996
		WO 9604323 A	15-02-1996
		WO 9604321 A	15-02-1996
		ZA 9506456 A	14-03-1996
US 4994534 A	19-02-1991	AU 620736 B	20-02-1992
		AU 6316190 A	11-04-1991
		CA 2026338 A	29-03-1991
		CN 1051737 A	29-05-1991
		EP 0422452 A	17-04-1991
		JP 1927993 C	12-05-1995
		JP 3217402 A	25-09-1991
		JP 6047606 B	22-06-1994
		KR 9506119 B	09-06-1995
		MX 22641 A,B	01-04-1993
		PT 95453 A	22-05-1991
		TR 24892 A	01-07-1992
		US 5304588 A	19-04-1994